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RESEARCH AND DEVELOPMENT OF THE SILVER OXIDE - CADMIUM ELECTROCHEMICAL SYSTEM

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PURPOSE

The purpose of this program is to investigate electrode reactions which take place in a sealed silver oxide-cadmium cell. In addition, the scope of this work includes a study of methods for improving the performance characteristics and reliability of the system for spacecraft use. At the conclusion of the contract 30 cells containing improvements in construction based on the findings during the investigation will be delivered to NASA for evaluation.

ABSTRACT

The effect of temperature on voltage and capacity is being investigated over the range of +40 to -10°C. Only minor variations in performance have been found when cells are charged and discharged in the range from 10°C to 40°C. It has been found that when cells are charged at "room temperature" and discharged at -10°C a voltage "dip" is exhibited by the cathode. However, when the discharge is preceded by a charge at low temperature (i.e. below 5°C) no voltage dip is encountered. When cells are cycled at minus 10°C the electrical efficiency (AHo/AHi) is the same as when cells are cycled on a room temperature charge -10°C discharge regime. However, the capacity is about 15% poorer.

Two sealed cells which feature 3 turns of fibrous visking casing with a nylon-dynel positive separator have completed 2100 cycles on the 100 min. regime. A recent deep discharge showed that the cells are performing somewhat better than two control cells fabricated with 5 turns of C19 in combination with a nylon positive separator.

A sealed five-cell battery which contained improved "ruggedized" cadmium electrodes and low density silver electrodes of increased geometric area, and an absorbent positive separator (i.e. no free electrolyte) has been deep cycled over 420 times at rates equivalent to the short orbit regime. One cell was arbitrarily dissected to determine the capacities of the positive and negative. It was found that the positive and negative lost about 15% and 5% of their respective original capacities. Standard positive and negative plates lost about 20% and 50% of their respective capacities when cycled on similar regimes.

Several cells which were constructed with impregnated cadmium electrodes in a porous silver matrix have completed 380 deep cycles before shorting. Results show that the active material utilization is 18% better than standard sponge negatives and comparable to cadmium impregnated nickel electrodes.

The problem of Cd inactivation with cycling and relatively poor electrical efficiency of active material is under investigation. In order to study the effect of separator debris on Cd inactivation, single negative electrodes were "dummy" cycled in electrolyte containing the oxidized and unoxidized solubles of either C-19 or PVA. Data after 600 cycles show that 10% less capacity is obtained from cells containing oxidized debris than from cells containing unoxidized debris and "clean" electrolyte. Surface area measurements indicate that a possible mechanism for the observed poorer capacity in these electrodes is reduction in electrode-electrolyte interface caused in part by reaction of cadmium with oxidized organic salts. Several approaches were investigated for improving the electrical efficiency of cadmium. These include CdO powder with increased surface area, expanders, and plastic binders. Cycle data from cells fabricated with high surface area CdO show about 12-15% better capacity than the controls after 250 cycles. CdO electrodes which contain a plastic expander and are of ruggedized construction show the best capacity maintenance. Cadmium electrodes "doped" with Fe_2O_3 exhibit about 10% better material utilization at -10°C than untreated electrodes. Negative electrodes fabricated with MgO and nickel stearate expanders also show slightly better performance at low temperatures. It has also been found that the wet-proofing properties of nickel stearate substantially increase oxygen recombination during overcharge.

Several specially designed 5 cell batteries which were initially charged to 65% of theoretical cadmium show no hydrogen evolution after 160 days of float at 7.75 volts.

BODY OF THE REPORT

1. PHASE 1. - Cell Tests

1.1 Effect of Temperature on Cell Performance

To study the effect of temperature on capacity and voltage maintenance four cells with two types of wraps were constructed. In one pair the wrap was 5 turns of C 19 with Pellon on the positive and negative electrodes; and in the other was two turns of fibrous Viskiag with a turn of Pellon on each positive and negative. One cell of each type contained 42% KOH and 38% KOH. Following several formation cycles the cells were fitted with Hg/HgO reference electrodes and cycled at 15 ma/in^2 charge and 100 ma/in^2 discharge over the temperature range of 40 to -10°C. Two additional cycles were also carried out, employing a constant current charge at room temperature and discharges at -10 and 0°C. Particular objectives were to determine the voltage, coulombic efficiency (AHo/AHi) and capacity in comparison to cells charged as well as discharged at those respective temperatures. Several YS-5(S)-4 cells were chosen as controls and also cycled simultaneously with the test cells. The performance characteristics of the cells over the temperature range of 40 to -10°C are shown in Figures 1-4. The capacities of test cells charged at room temperature and discharged at various temperatures from 40 to -10°C are also shown in the figures (indicated by the dash line.

It can be seen from Figure 1. that the capacities of the test cells are about one ampere hour better than the standard design over the entire temperature range. The test cells fabricated with fibrous Viskiag cellulose show somewhat improved capacity at -10°C as compared with the cells fabricated with C-19.

This is due in part to the lower resistance of the multi-layers of Visking compared to C-19 (i.e. .03 ohms compared to .05 ohms). The comparison of the above capacity data with results obtained from cells charged at room temperature indicate that discharge performance above 10°C is similar. When the discharge temperature was decreased below 10°C the cells charged at room temperature showed 11 and 14% better capacity at 0 and -10°C respectively than did cells charged at these lower temperatures. Since the discharge regime for all the cells was the same, it follows then that the poorer capacity observed for the cells charged below 10°C was caused by an inability of the silver electrode to efficiently accept charge. This inefficiency may be caused in part by reduced mobility of OH^- ions in the KOH electrolyte at low temperatures (higher KOH viscosity), which in turn results in poor OH^- diffusion through the separators to the positive electrode.

Figure 2. shows deep discharge curves for cells cycled at 0 and -10°C respectively; the dash lines represent cells charged at room temperature. The results clearly indicate that again the capacities of the cells charged at room temperature are somewhat superior. (i.e. 12-14%) However, it can be seen that the cells which were charged at room temperature did not exhibit a "normal" AgO plateau on discharge. In fact a voltage dip of 30-40 mv below the Ag_2O plateau was evident during the initial portion of the discharge. The cells which were charged at low temperatures retained their AgO capacities. The coulombic charge efficiency of the silver electrode is reduced at low temperatures during the portion of the charge

$$2Ag + 2OH^- \longrightarrow Ag_2O + H_2O + 2e^-$$

The inefficiency is probably related to an increase in IR of the silver electrode which results in a rise of the ohmic overpotential during charge. It follows that a longer percentage of the charge than is normally observed on the AgO plateau at room temperature is obtained at lower temperature. Therefore, the amount of metallic silver contained in the positive electrode at the end of charge at low temperature probably is greater than for an electrode charged at room temperature. Hence, the voltage "dip" observed during discharge at low temperatures (following a room temperature charge) is attributed to a high concentration of Ag_2O in the electrode and more specifically Ag_2O adjacent to the grid. Improvement in the performance of the silver electrode at low temperature by "doping" of the plate is presently under investigation in a company supported program.

The effect of temperature on the voltage characteristics of the Ag-Cd couple and the silver electrode alone are presented in Figures 3 and 4 respectively. It can be seen that the cells fabricated with Visking in combination with 38% KOH exhibit the highest discharge voltages at all temperatures and particularly at -10°C. At this temperature the plateau voltage is about 30 mv higher than cells with C-19 and 42% KOH. The voltage on charge however, is nearly equal because the resistance of the separators and electrolyte was not significant at the low current density used.

1.2 Effect of Separator System on Cell Performance

Four cells were built with either C-19 or Viskíng main separator and woven interseparators in order to study the effect of these materials on cell performance characteristics. The cells contained positive electrodes pressed to a density of 4.2 g/cc and standard CdO negatives. All cells were activated with 42% KOH. To accelerate the evaluation, the cells were cycled at rates equivalent to the 100 minute orbit regime. The cells were charged at 1.7A to 1.65 volts (or 65 minutes, whichever came first) and discharged at 3.0A for 35 minutes on each cycle. The cells were given a deep discharge every 250 cycles to determine their capacity. Two additional cells were built with (+) 1 Pellon -6 mil/3 Viskíng/ (-) / 1 Pellon - 6 mil and contained no "free" electrolyte. At present the first group of cells has completed 2100 cycles and the second group has completed 750 cycles.

The results presented in Figure 5. show that the cells fabricated with Viskíng are maintaining about 16% better capacity than the cells made with C-19. It can further be seen that the removal of free electrolyte (i.e. cells containing Pellon) does not significantly decrease cell performance.

In order to accrue additional information regarding the over-all merits of Viskíng and C-19 several 5-cell batteries of the above design along with 5 cell batteries containing "ruggedized" wet-proofed cadmium electrodes have also been constructed. The design parameters for these batteries are given in Table I. It should be noted here that a standard YS-5(S) battery was omitted from this series, in view of the fact that sufficient data are available for comparison with the batteries under test.

The cells, prior to being assembled as batteries were filled with an excess quantity of 42% KOH and allowed to soak for 72 hours. The cells were first charged at 300 ma to 65% of theoretical cadmium capacity and discharged at 1.0 amps to 0.6 volts. The second charge was carried out at 300 ma to 1.58 volts, after which time all the free electrolyte was removed. The cells were assembled as 5-cell batteries, fitted with pressure gauges, and sealed. The batteries were then subjected to evaluation cycling at 40°C, "RT", and -10°C, at charge and discharge rates of 1.7A and 3.0A respectively. After the charge at each temperature the batteries were overcharged until the first cell reached 60 psia. Charge was stopped and the pressure was allowed to decay. The recombination rate for this period was calculated as dp/dT as a function of pressure. The evaluation cycle data are given in Table II.

The results indicate that the batteries which were fabricated with "ruggedized" cadmium electrodes and low density silver plates, (i.e. Batteries C and D) are performing about 5% better than Battery A on an ampere hour basis at room temperature. However, it should be remembered also that these batteries contain about 15% less silver than Battery A; therefore, the overall increase in performance based on silver content is about 20%.

This better performance may be attributed to the low density silver electrodes which have been shown to increase charge acceptance at high rates by providing more electrode-electrolyte area for anodization than do denser electrodes.

At -10°C the significance of higher ratio of cadmium to silver and lower resistance separator system becomes evident. Specifically, it can be seen that the performance of Battery D (Visking separator and 1.5:1.0 cadmium to silver) is about 23% greater than Battery A (C-19 separator and 1.3:1.0 cadmium to silver). Moreover, comparison of the low temperature data from Battery A and Battery B indicates that increasing the cadmium to silver ratio to 1.5 and eliminating non-working negative material from the end negatives (use of half end negative plates) gives the greatest increase in performance during early cycles.

Battery cycling equipment is under construction for life evaluation of these units on the 100 minute regime. Additional equipment is also being fabricated which will cycle similar batteries on the 24 hours orbital regime.

2. PHASE 2. Gas Recombination

2.1 Effect of Cadmium Surface Area on Oxygen Recombination

A parameter that is known to affect oxygen recombination is the area ratio of gas-liquid-solid on an electrode for oxygen consumption. It would be important therefore to determine if cadmium with increased surface area shows improved oxygen recombination properties.

To study the effects of surface area on gas recombination special CdO & $Cd(OH)_2$ powders of different particle size were prepared. The method of preparation was similar to that which was described in the First Quarterly Program Report and discussed in section 3.4. Briefly, the powders used for this study were prepared essentially by three methods: (1) sieving of standard CdO powder through 200 mesh screen.(2) precipitation of $Cd(OH)_2$ from the nitrate salt in hot 31% KOH (60°C) and subsequent thermal decomposition to CdO and (3) thermal decomposition of cadmium acetate at 350°C. The surface areas of the powders were then measured using the Numinco Surface Area-Pore Analyzer. The values are given below:

Sample	Surface Area m^2/g
standard CdO	1.3
method (1)	1.65
" (2)	5.9
" (3)	9.0

The cadmium powders were pressed into electrodes to a density of 2.8 g Cd/cc. They were then assembled into individual five ampere-hour (nominal) cells. The design of the cells was such that maximum rates of recombination were achieved without damaging cell performance (i.e. Pellon

interseparator system with maximum electrolyte removal). The cells were initially charged at 300 ma to 65% of theoretical cadmium capacity, and discharged at 1.0 amp to 0.6 volts. Following the second charge the free electrolyte was removed, and the cells were then fitted with pressure gauges and sealed in epoxy. In order to simulate the condition on short orbit the cells were overcharged at 1.0 A to a pressure of 60 psia. The cells were then placed on stand and the rate of oxygen recombination was plotted as log dp/dT versus log P. The results of the overcharge and stand tests are presented in Figures 6, and 7 respectively.

Figure 6 shows that the cell fabrication with CdO at 5.9 m^2/g gives the best overcharge characteristics. Specifically, an improvement of about 40% is obtained on overcharge compared to the cell made with standard CdO. It is also of interest to note here that the CdO with the greatest surface area (i.e. 9.0 m^2/g) demonstrated a somewhat faster rate of pressure build-up than the CdO of 5.9 m^2/g. The failure of the cell to give good oxygen recombination as well as better performance is not understood. It was found that extremely high pressures were needed to bring the electrodes to their correct density. This may have produced a plate with a dense surface and a more porous interior, thus actually reducing the number of active sites available for recombination. There is evidence for this in that the surface of these plates showed metallic luster.

Referring now to Figure 7, it can be seen that the active material at 5.9 m^2/g gave the best rate of oxygen consumption. At 60 psia the rate was about 30% better than the standard electrodes and at 15 psia it was about 37% better.

The electrodes made from 9.0 m^2/g CdO again showed about 25 % poorer oxygen recombination than the electrodes of 5.9 m^2/g. The poorer recombination observed for these electrodes in consistant with the poorer capacity obtained during cycle tests. The results are discussed in section 3.4 of this report.

3. PHASE B.

Investigation of Negative Electrode Efficiences

Both pasted and pressed CdO Electrodes accept 85-96% of theoretical capacity on the first charge (depending on the current desity) before gassing. However, only 60-65% of the input is delivered on the subsequent discharge. This coulombic inefficiency may be due to: 1) poor conductivity of the discharge products; 2) poor conductivity between the grid and active material, and/or 3) lack of porosity or real surface area of the CdO electrodes, resulting in poor diffusion of OH^- in the plate during discharge. Most important is the problem of maitianing good utilization for extended periods of cycling; it has been found that as much as a 50% loss in capacity can occur after several thousand shallow cycles. These and related problem areas are presently being studied.

3.1 Effect of Grid Structure

Data accumulated during the last quarter showed that supported cadmium electrods (in a nickel matrix) gave about 15% better utilization of active material after prolonged cycling than sponge electrodes. This may be due to the increased conductivity between the grid and active material and also the relatively smaller crystal size of the impregnated Cd which probably results in a higher surface area.

Since many NASA space missions, however, require the use of non-magnetic components on board the satellite, nickel plaques of course cannot be used. To eliminate the undesirable magnetic effect of nickel, cells were constructed with negative electrodes in which the active material was impregnated into a silver matrix. The silver plaques were fabricated by mixing a fine

silver powder with sodium chloride, pressing the mixture to the proper density, sintering the plates for 10 minutes, and leaching out the salt in water. The plaques obtained were 85% porous. The plates were impregnated with a saturated solution of $Cd(NO_3)_2$ until the final impregnated weight corresponded to a plaque loading of about 40% (based on $Cd(OH)_2$). The electrodes were then assembled into two cells containing 4 positives and five negatives. The separator system was (+) 1 Pellon-6 mil /6C-19/(-)/ 1 Pellon-6 mil; the cells contained 42% KOH. An additional pair of cells was also constucted with standard sponge negatives and similar separatos and electrolyte. The sponge negative cells contained the same wieght of cadmium as the cells containing impregnated negatives.

Following several formation cycles the cells were deep cycled at 65 ma/in^2 charge and 100 ma/in^2 discharge at 40°, RT, and -10°C to determine the performance characteristics of the impregnated electrodes. The results, summarized in Table III shown below consist of averages for each pair of cells. Data for cadmium impregnated nickel plaques are also presented for comparison.

TABLE III

Cadmium Impregnated Ag Electrodes Deep Cycle Performance Data

Temperature	40°C		RT		-10°C	
Electrode Type	gCd/AH	*Cd Volt.	g/Cd/AH	*Cd Volt.	gCd/AH	Cd Voltage
Sponge	3.23	0.84	3.37	0.84	4.55	0.82
Cd Impregnated Silver	3.15	0.85	3.20	0.85	4.00	0.83
Cd Impregnated Nickel	3.28	0.85	3.15	0.85	4.05	0.83

* Vs Hg/HgO reference electrode

The results show that the active material utilizations for both types of impregnated electrodes are about equal at all temperatures. The total utilization (active material plus plaque) of the sintered nickel plaque electrode, however, is 25% poorer than the sintered silver plaque, due mainly to its lower porosity (i.e. the density of the sintered nickel plaque before loading was about 2 g/cc, while the silver plaque was only 1.5 g/cc.) The results also clearly indicate that the impregnated electrodes gave 12% better capacity at low temperatures during initial cycles than the sponge electrodes.

Following the evaluation cycling the cells were fitted with pressure gauges and sealed in epoxy. The cells were overcharged at 65 ma/in^2 to 60 psia, and the oxygen pressures were then allowed to decay. The recombination rates on stand are presented in Figure 8. The results show that both types of impregnated electrodes exhibit 40% better recombination than the sponge electrodes at 60 psia and about 30% better at 15 psia.

The cells were then placed on a deep cycle regime at 1.7 A(83 ma/in^2) charge and 3.0A (150 ma/in^2) discharge. The capacity maintenance data for 400 cycles for these type of electrodes are shown in Figure 9.

The results show that the cells fabricated with supported electrodes after 400 cycles were delivering about 30% better capacity. However, based on the total electrode weight the utilization of the sponge electrodes was slightly superior to the sintered nickel plaque and about equal to the sintered silver plaque. It can be seen from these results that it is thus possible to construct a sealed cell with the required non-magnetic properties without losing the benefits afforded by the sintered matrix structure.

Cognizance should be taken of the fact that although supported cadmium electrodes are superior to conventional sponge electrodes for maintaining capacity, even better performance has been obtained with sponge electrodes which contain a plastic binder in combination with a fibrous matrix. These results will be discussed in section 3.2 of the report.

3.2 Development of a "Ruggedized" Cadmium Electrode

During the evaluation of wet-proofing additives to the negative electrode (to increase oxygen recombination), it was found that their plastic properties also added considerable strength to the plate. However, without any additional binders the plate developed severe cracks during cycling. It was therefore necessary to provide the electrode with additional strength by the addition of a fibrous matrix. The function of the plastic binder thus became to interlock the cadmium oxide particles around the fibrous matrix; it was found that this combination greatly increased the mechanical strength of the electrodes. Specifically cadmium oxide electrodes with a rigid structure were prepared by incorporation of 2.5% plastic binder along with 0.15% fibers in the active material. When prepared with proper amounts of water it was found that the CdO-binder-fiber mix formed a putty like mass which could be rolled on a conducter and then cut to proper plate size. If no water was added the electrodes could still be pressed, although with some difficulty, to the correct density.

Several "ruggedized" electrodes were first deep cycled in partial cells to determine how the electrodes maintain capacity during prolonged

cycling. The rates of charge and discharge used were equivalent to the short orbit regime. The results after 400 deep cycles show that the ruggedized Cd electrode was still delivering 90% of its original capacity (i.e. .277 AH/g cadmium), while the standard electrodes capacity had decayed to 50% of its original output (i.e. .16 AH/g cadmium). BET surface area measurements showed that the new electrode actually increased about 5% in area from 6.2 m^2/g to 6.55 m^2/g after cycling, while the control electrodes area decreased from 5.95 m^2/g to 4.6 m^2/g after the same number of cycles.

Following this experiment a five-cell battery was constructed which included in its design plastic bound-fibrous negatives, along with low density silver electrodes, one Pellon (polyamide) on the positive and negative and two Visking (fibrous) casing as the main separator. The battery was also evaluated on a rapid deep cycle regime. The capacity maintenance of the battery compared to the standard design is shown in Figure 10.

The capacity data clearly shows that the "ruggedized" design was giving 5.5 AH after 420 cycles, while the control had dropped to 3.8 AH or a loss in capacity of about 40% based on initial output. One cell from the test battery developed a short at cycle 420 and was dissected; for comparison a standard cell was also dissected. Visual observations indicated that the cause of failure of the test cell was separator attack by silver. The negative electrodes retained their original mechanical strength. The standard negative electrodes, however, had cracked in several places, and had also decreased 1/16" in width. One positive and one negative electrode from each cell were then assembled into "dummy cells"

and filled with fresh electrolyte to determine electrode performance; the results are presented below in Table IV.

TABLE IV

Single Electrode Performance
after 420 deep cycles

8.5 g Cd/plt — Ic = 83 ma/in^2, Id = 150 ma/in^2

5.85 g Ag/plt (new)
4.5g Ag/plt (after 420 cycles)

	AHo	gCd or Ag/AH
positive electrode (test cell)	1.55	2.92
positive electrode (std cell)	1.52	2.95
negative electrode (test cell) (raggedized)	2.42	3.50
negative electrode (std cell)	1.17	7.25

The data show that the plastic binder-fibrous negatives were delivering over 100% better capacity than the standard negatives. The capacities of the two positive electrodes, however, were about equal. The loss in capacity of the test cell can be directly related to the loss in silver from the positive electrode to the separator. Specifically, the positive electrode lost 23% of its silver to the separator. Although the loss in active material from the standard cell was the same the capacity was 1.7 ampere-hours poorer. This poorer capacity must be due to the negative electrode.

The improved utilization of the ruggedized negative electrode may be due in part to the fact that the wet-proofing binder decreases the KOH electrolyte retention of the plate by about 18%. It is obvious then that the quantity of oxidized soluble separator debris which is known to decrease Cd utilization, is also substantially reduced. The binder-fiber-combination also prevents cracking of the electrode which is probably due to densification and shrinking of the metal with cycling. This shrinkage has also been found to decrease the utilization of cadmium.

3.3 Effect of Additives to the Negative Electrode

In studying the performance of pressed CdO electrodes, large capacity losses with cycling have been observed. Data indicate that there are several distinct "aging" processes occurring on the cadmium during cycling. One is the partial inactivation of plate caused by formation of $CdCO_3$ and other low molecular weight organo-metallic salts. This phenomenon will be discussed in section 3.5 (Effect of Separator Debris on Cadmium Utilization). Probably most important, however, is the inactivation of the Cd metal caused in part by densification and re-crystalization of the metal. It is also likely that the separator debris is affecting the crystal habit of the metal. Several researchers have found that "expanders" greatly decrease the loss of capacity on the cadmium electrode with cycling. Rosenzweig et al (Extending the Life of the Negative Electrode of Alkaline Batteries U.S.S.R 108,799-1958) claims that high molecular weight organic acid and alkohols will improve the performance of the cadmium electrode. Winkler (Alkaline Batteries with Negative Cadimium Electrodes Ger.-East 12,053 Aug 1956) claims that small percentages of MgO or $Mg(OH)_2$ added to the cadmium powder will prevent the loss of cadmium utilization. Moultor (Alkaline Storage Cells with Cadmium Type Neg. Electrodes U.S. 2,870,230 Jan 1959) claims

the same with 1% polyvinylpyrrolidone. In accordance with these findings the above additives were investigated along with Fe_2O_3 and nickel stearate for use in prolonging the life of sealed cells.

Eight five ampere-hour cells were fabricated with various percentages of these additives, filled with 42% KOH, given five cycles at room temperature at various discharge rates, and then sealed. They were then given several deep cycles at 40°C, RT, and -10°C at rates equivalent to the 100 minute orbit regime. The cells were then placed on the 100 minute life cycle regime discharging 35% of nominal capacity in 35 minutes. The deep cycle performance data after 600 shallow cycles are presented in Table V.

The early cycle data show little difference in capacity among the cells containing various additives. However, at -10°C the cells which contain Fe_2O_3 exhibited about 10% better capacity on discharge than the control cell. The other additives either did not benefit cell performance, or adversely affected the capacity (i.e. 5% nickel stearate). At cycle 600 the cells were again given several deep discharges, and as can be seen, none of the additives afforded any increase in cell capacity. It can further be seen that the cells containing 5% nickel stearate and 20% Fe_2O_3 were giving 13 and 10% poorer capacity respectively, than the control.

Since the overall objectives in this phase of study are to improve the utilization of the negative electrode, the cells will have to be cycled till failure so that the cadmium electrodes can be evaluated after prolonged cycling independently of the cell.

The cells prior to being placed on the cycling regime were tested for oxygen recombination. It was found that the additives with the exception of 5% nickel stearate did not affect the rate of oxygen consumption. The cell containing 5% nickel stearate showed a remarkable ability to accept substantial rates of overcharge.

The improved rate of recombination may be attributed to the wetproofing properties of the nickel stearate. The compound was not hydrolyzed, or for that matter even wetted after 30 days in contact with 42% KOH at room temperature. Some hydrolysis did occur when the compound was boiled in strong alkali. The data for the overcharge and stand tests for the cell containing 5% nickel stearate are shown in Figure 11.

At 5 ma/in^2 a "steady state" pressure of 44 psia at a voltage of 1.65 after 65 hours of overcharge is attained. The control reached 70 psia after 15 hours and had to be discontinued. At 15 ma/in^2 a steady state pressure could not be reached with either cell because the pressure rose too rapidly. However, the test cell was able to accept about 6 times as much overcharge before reaching the 60 psig pressure limit. After 600 shallow cycles the oxygen recombination rates were again determined. It was found that the cell containing 5% nickel stearate had lost about 50% of its initial overcharge capabilities; the control had lost about 35%.

Further work is planned with this rather interesting compound to determine how it facilitated recombination. Several larger size cells (i.e. 16 ampere-hour) containing this additive will also be constructed in order to learn if similar overcharge current densities can be imposed.

3.4 Effect of CdO Surface Area on Cadmium Utilization

A parameter that is known to affect cell performance is the real surface area of the electrode. During the last investigation period it was found that during initial cycles a linear relationship exists between utilization and surface area in the range of about 1-5 m^2/g. Specifically the cadmium utilization was 63% of theoretical at 1.5 m^2/g and 75% of theoretical at 4.5 m^2/g during initial cycles. As a result of this preliminary investigation, full size 5 ampere hour (with a 1:1 Cd to silver ratio) were fabricated and to date have completed 250 cycles to 35% depth of discharge on the 100 minute orbit. The results are given in Table VI. below

TABLE VI

Effect of CdO Surface Area on Negative Plate Utilization

CdO Surface Area - m^2/g	Cd Utilization - g/AH	
	Initial	250 cycles
1.3	3.35	3.73
1.65	3.25	3.75
4.5	2.8	3.35
5.9	2.72	3.41
9.0	3.20	3.97

After 250 cycles the CdO electrodes made from powders of 4.5 and 5.9 m^2/g are exhibiting about 10% better active material utilization than the electrodes made from commercially available CdO at 1.3 m^2/g. The electrodes fabricated from powder at 9.0 m^2/g showed somewhat poorer utilization, probably due to the high pressures needed to press the electrodes initially, as explained above.

The number of data are as yet insufficient to establish the overall merits of increasing the surface area of CdO. It will be of particular interest to learn how these electrodes behave during more extended cycling.

3.5 Effect of Separator Debris on Cadmium Utilisation

In order to study the effect of separator debris on cadmium inactivation single CdO electrodes of standard construction were dummy cycled on the short orbit regime. The electrolytes in which the plates were tested contained the oxidized and unoxidized solubles of either C-19 or PVA. The oxidized debris was prepared by reacting a saturated solution of Ag_2O (containing excess solid Ag_2O) in 42% KOH with either C-19 or PVA separators. The separators were allowed to remain in contact with the solution for 48 hrs. at room temperature. The supernatent liquid was then decanted and filtered directly into the cells. The unoxidised debris was prepared in a similar manner but the solubles were extracted in the absence of Ag_2O. To determine the quantity of separator debris present in the electrolyte, the leached separators were washed free of alkali, dried, and weighed. It was found for separators soaked in KOH plus Ag_2O that 6% by weight oxidised soluble material had dissolved in the electrolyte. The separators soaked in KOH only, had lost 3% to the electrolyte. The cells were initially charged to 75% of theoretical cadmium capacity. They were then given several deep cycles at 50,100, and 200 ma/in^2 discharge rate; the charge rate was kept constant at 20 ma/in^2. Following the evaluation cycles the cells were sealed in polyethylene bags to prevent additional carbonation by air, and placed on the short orbit regime at 65 ma/in^2 charge and 100 ma/in^2 discharge.

At cycle 600 the cells were given several deep discharges at the above three rates. The results are given below in Table VII.

TABLE VII.

Effect of Separator Debris on Cadmium Utilisation

Electrolyte-Type	Cd Capacities - Ampere Hours					
	Initial cycles			600 cycles		
	50 ma/in^2	100 ma/in^2	200 ma/in^2	50 ma/in^2	100 ma/in^2	200 ma/in^2
Unoxidised C 19 debris	1.43	1.40	1.30	1.03	0.98	0.88
Oxidised C 19 debris	1.46	1.33	1.18	0.96	0.89	0.74
Unoxidised PVA debris	1.48	1.39	1.27	1.06	0.95	0.84
Oxidised " "	1.37	1.24	1.13	0.92	0.83	0.75
Pure 42% KOH	1.45	1.40	1.32	1.05	0.92	0.88

WT of Cd = 4.75 g/plt.
density = 2.8 g/cc
Area = 4.9 in^2

The data after 600 cycles show that about 10% poorer capacity is obtained from cells containing oxidised separator debris as compared with cells containing unoxidised debris and "clean" electrolyte. Cognisance should be taken of the fact that although the absolute capacity values for the electrodes are different, all plates decreased about 33% from their respective initial capacities. These results indicate that although oxidised debris has a greater effect in reducing the capacities of the cadmium electrodes than unoxidised debris, a more severe decrease in utilisation occurs through densification or "aging" of the metal, possibly by re-crystalisation.

The cells were dissected after 600 cycles and the surface areas of the cadmium plates were measured by BET. The data are summarised in Table VIII. below.

TABLE VIII.

Surface Area Measurements of Cycled Cd - Electrodes

Electrode Type	Initial Surface Area	Surface Area after 600 cycles
Cd cycled in pure 42% KOH	5.9 m^2/g	5.65 m^2/g
" " " unoxidised C-19	6.0 " "	5.55 " "
" " " oxidised C-19	6.3 " "	5.0 " "
" " " unoxidised PVA	5.7 " "	5.6 " "
" " " oxidised PVA	6.0 " "	4.9 " "

It can be seen that the electrodes cycled in pure 42% KOH in unoxidised separator debris lost between 1.5 and 6% of their surface area, while the electrode cycled in electrolyte containing oxidised C-19 and PVA debris lost 20 and 18% of their surface area. These results indicate that a possible mechanism for the observed poorer capacity may be reduction in electrode-electrolyte interface, caused in part by reaction of cadmium with oxidised organic salts and densification of the Cd metal.

At the conclusion of the cycle tests the electrodes will be analyzed by election microscopy to determine how the separator debris affects the crystal habit of cadmium.

4. PHASE 4.

Prolonged Constant Potential Charging

The problems of hydrogen evolution, and cell unbalance (variations in individual cell voltages from the mean battery voltage) during long periods of "float" are under investigation in this phase of the program. The gassing problem is being studied both in multi-cell batteries and in single cells. The problem of cell unbalance obviously is a multi-cell phenomenon and is being studied as such. The study was initiated with the use of two 5-cell batteries which contained Pellon on the positive and negative electrodes and were charged to a low extent of negative formation on the first charge. The cells in each battery contained no "free" electrolyte. The batteries were then given five evaluation deep cycles, fitted with pressure gauges, sealed in epoxy, and placed on constant potential charge at 7.75 volts (1.55 v/cell). Periodically the batteries were given a deep discharge and then returned to float. When pressure increases became significant, gas analyses were also performed. At present the batteries have been on float for 160 days. An additional 5-cell battery which was initially charged to 65% of theoretical negative capacity, consisting of standard YS-5(S)-4 cells was also put on constant potential charge for comparison with the other two units. It has been on float for 90 days. The pressure, voltage, and capacity data for all three batteries are presented in Table IX.

Results after five months on float from the batteries containing Pellon show that maximum voltage variation is within 80 mv at a nominal float voltage of 7.75 volts. These results are in sharp contrast to data

obtained from standard cells which show a spread of as much as .25 volts after only three months on float. Most important is the fact that gas analyses showed that these batteries did not show any hydrogen on float, whereas the standard design with an equal degree of formation began to evolve hydrogen after 40 days on float.

It is significant that the high pressures initially observed in Battery G (charged to 65% of theoretical Cd and contained nylon inter-separators) were due exclusively to oxygen. No pressure decay was noted in this battery until about day number 40 at which time 10% hydrogen was found in cell #3. This cell also showed the most rapid pressure decay during subsequent days on float. On day 50, 22% and 17% hydrogen was found in cells one and two respectively. The presence of hydrogen in these cells was found to be related to a voltage rise which occured between days 39 and 43. Specifically, the voltages reached about 1.67 volts while the remaining cells in the battery fell to about 1.43 volts.

It appears evident from these data that the primary mechanism for gas recombination in Battery G was the reaction of hydrogen with oxygen; probably catalyzed by the silver additive in the negative electrode. Some evidence of direct recombination of the two gases at the nickel sites of impregnated cadmium electrode has been reported by Seiger & Shair. The mechanism appears to be similar for sponge electrodes as well. However, since no evidence of hydrogen evolution in Batteries E and F has been found, it may be assumed that the pressure decay observed here is primarily due to direct recombination of oxygen with cadmium. It may be that Pellon allows access to the interior of the negative plate by oxygen,

whereas the nylon used around the negative electrodes in the standard cells impedes oxygen diffusion resulting in recombination only at the edges of the electrode. This absence of oxygen reaction with cadmium in the middle of the electrode would then cause hydrogen evolution, since the state of charge of the negative would be higher.

To determine if this is indeed the cause of hydrogen generation one cell from Batteries E and G will be dissected in an inert atmosphere. The negative electrodes will then be cut into sections and each portion analyzed for Cd and CdO content. It is expected that the analysis will show that the composition of the edges of the electrodes from the Battery G is mostly CdO, while the electrodes from Battery E, will have a more equal distribution of Cd and CdO throughout the plate.

In another experiment individual cells of both designs, initially charged to a low extent of cadmium formation, are being floated at potentials between 1.5 & 1.8 volts. The cells are fitted with reference electrodes in order to determine the exact cadmium potential at which hydrogen is evolved. Data thus far indicate no hydrogen generation below 1.60 volts or a cadmium voltage of 1.02volts for both designs. The results for floating at higher potentials will be presented in the next quarterly report.

Similar studies will also be carried out in cells where the extent of negative formation is higher than 65%.

Program for Third Quarter

Phase 1.

Study cycled cadmium electrodes by election microscopy to determine how cycling affects the crystal structure of the active electrode material. Investigate improvements in positive electorde characteristics at low temperatures, problem areas being improvement in material utilization and elimination of voltage "dip" on discharge (following a room temperature charge). Specifically, "doping" of the electrodes and electrolyte additives will be investigated. Study means of extending the life of the sealed Ag-Cd system to short circuit through use of newly developed Radiation Applications Inc. separator X2.2H. This study will include cycling tests of cells and batteires at temperatures from -10°C to 40°C.

Phase 2.

Study the rates of oxygen evolution and recombination as a function of cycle life. Determine the rates of oxygen recombination during overcharge as a function of current density for wet-proofed CdO electrodes.

Phase 3.

Continue the study on methods for improving the performance of the cadmium electrode. Investigation methods for fabrication of ruggedized plastic bound electrodes such as rolling, and extrusion, with a view to incorporation of either method into production of larger model sealed cells. Special attention will be paid to controlling thickness and weight which will result in reliable performance of the electrodes.

Phase 4

Continue the determination of the conditions leading to evolution of hydrogen during constant potential charging, with particular emphasis on determining the voltage at which hydrogen is evolved in cells with various degrees of negative formation. Analyze Cd electrodes after prolonged periods of float and determine composition of plate at various locations (i.e. edges, top & middle). Investigate float voltage and gas evolution also as a function of temperature.

EFFECT OF TEMPERATURE ON CELL PERFORMANCE

$I_C = 15 ma/in^2$ } CHARGE & DISCHARGE AT THE SAME TEMP.
$I_D = 100 ma/in^2$ }

AREA = $24.5 in^2$ 22g Ag/CELL

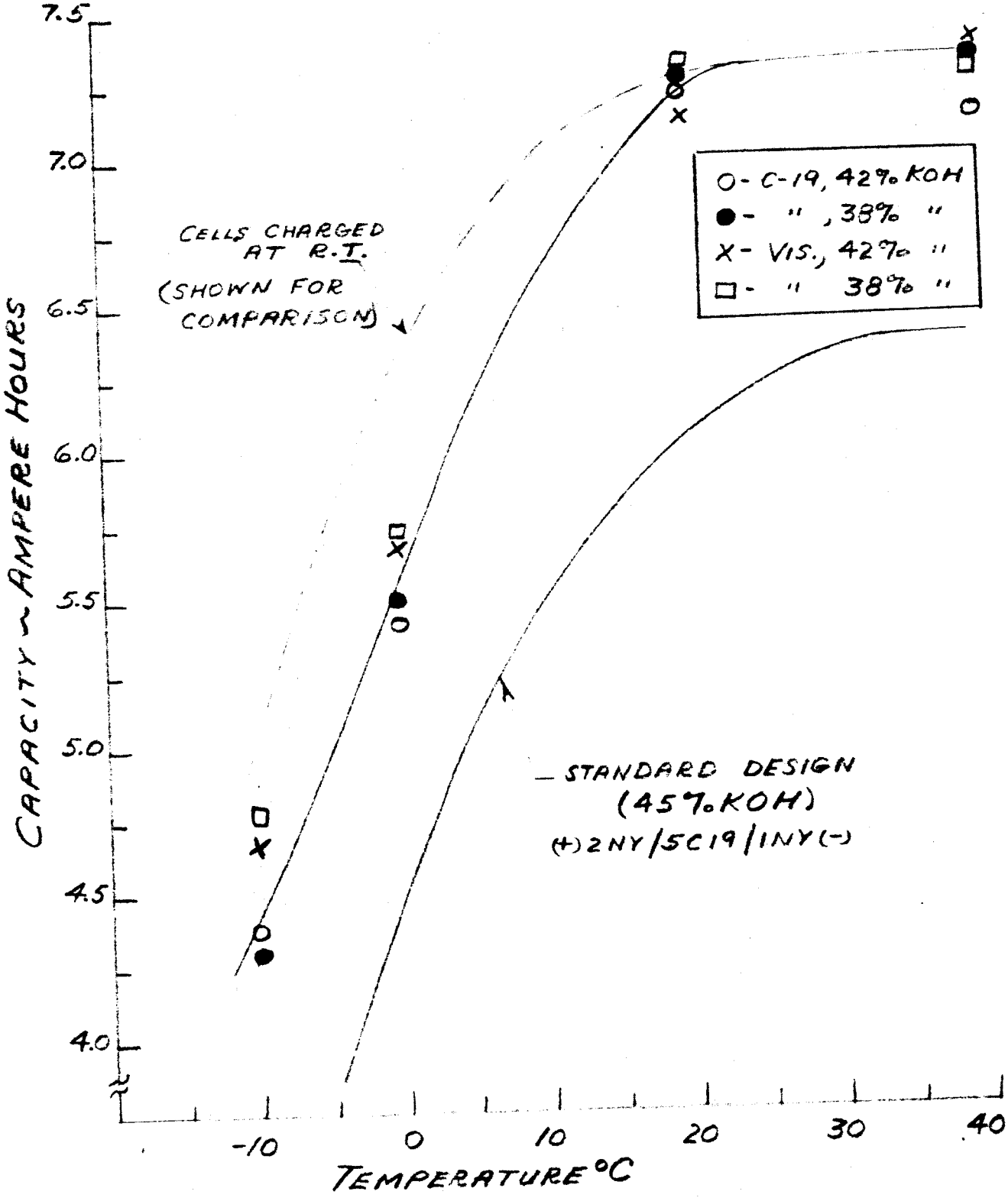


Fig. 1

LOW TEMPERATURE DISCHARGE PERFORMANCE DATA

$I_D = 100\ ma/in^2$

AREA = $24.5\ in^2$

SEPARATOR SYSTEM: 1P-6/5C-19/1P-6
42% KOH

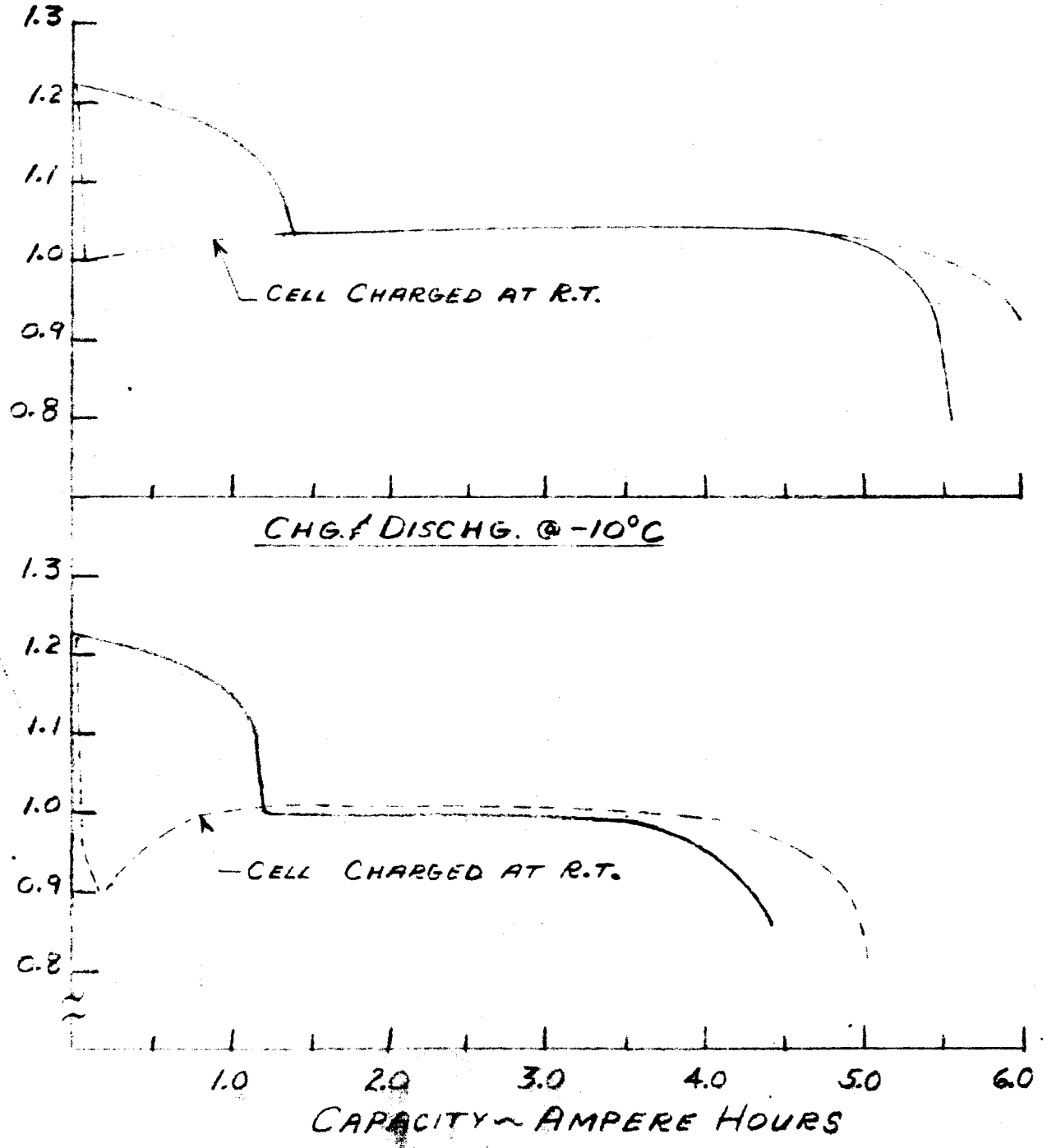


Fig. 2

EFFECT OF TEMPERATURE ON CELL VOLTAGE

$I_C = 15 ma/in^2$

$I_D = 100 ma/in^2$

$AREA = 24.5 in^2$

	SEP.	KOH
○ -	C-19	42%
● -	"	38%
X -	VISKING	42%
□ -	"	38%

——— DISCHG.

- - - - - - CHG

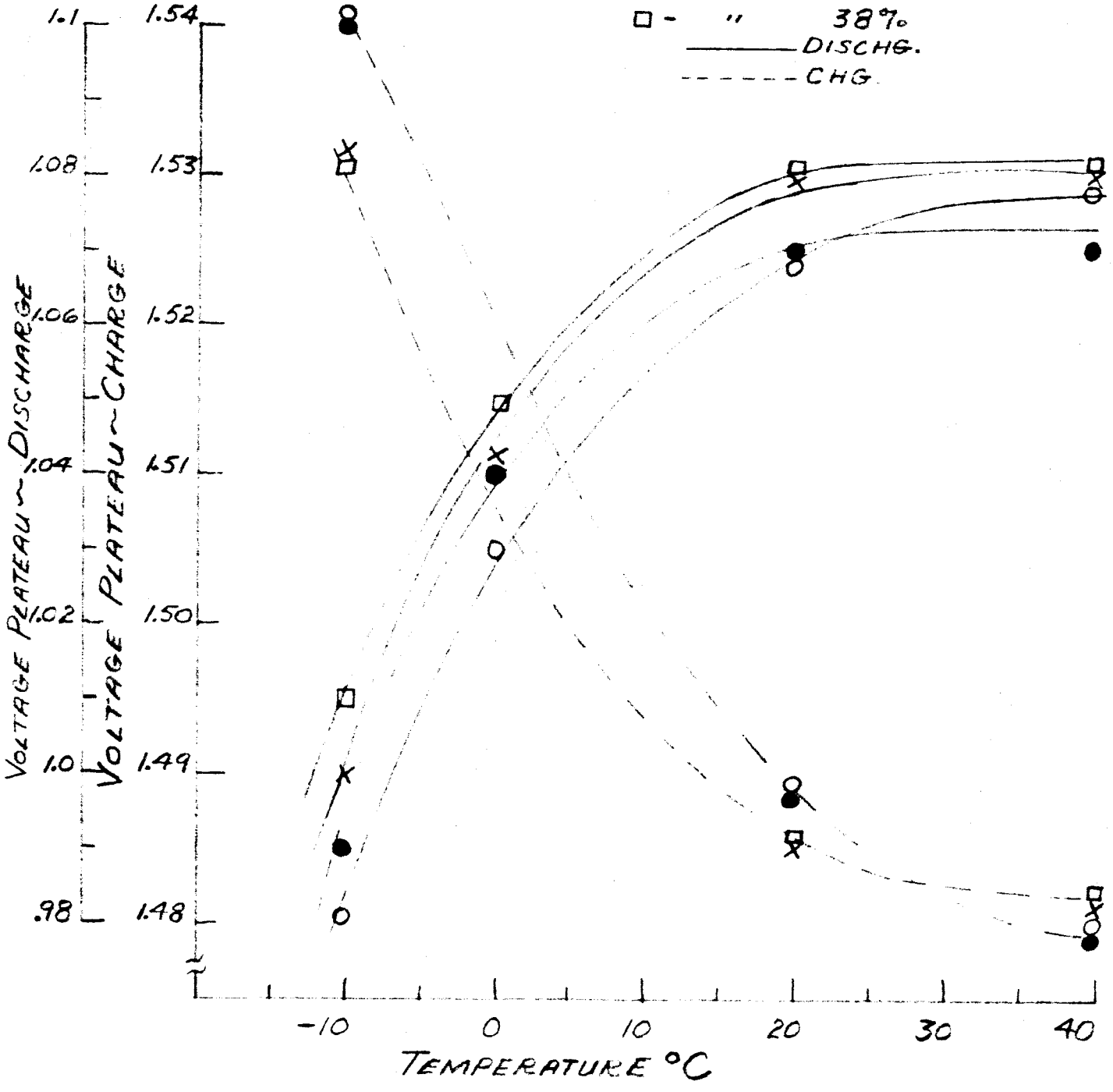


Fig. 3

POSITIVE ELECTRODE VOLTAGE CHARACTERISTICS

42% KOH

$I_D = 100 ma/in^2$

$AREA = 24.5\ in^2$

O - INITIAL VOLTAGE

X - PLATEAU "

- - - - - - CELLS CHARGED AT R.T.

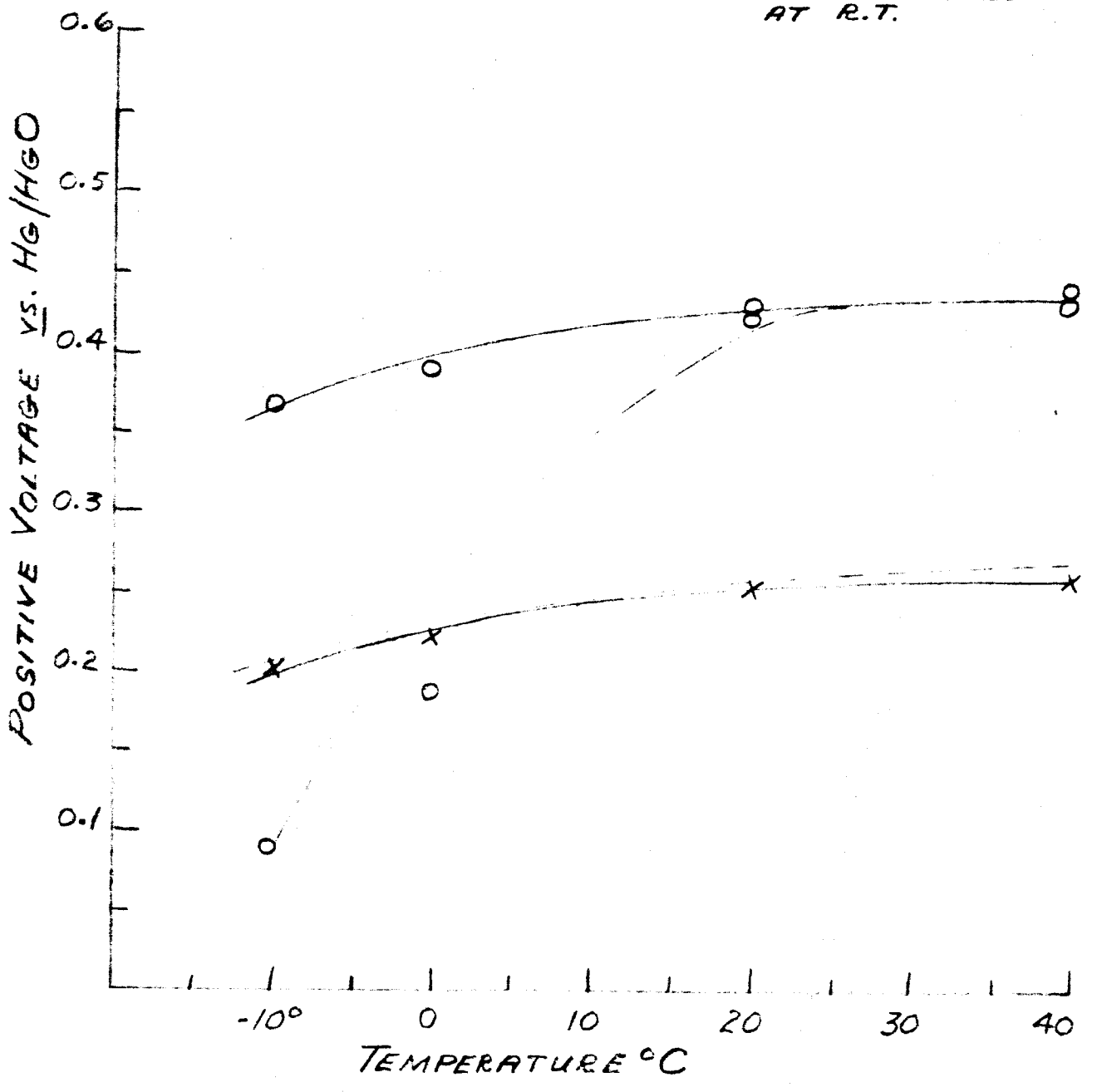


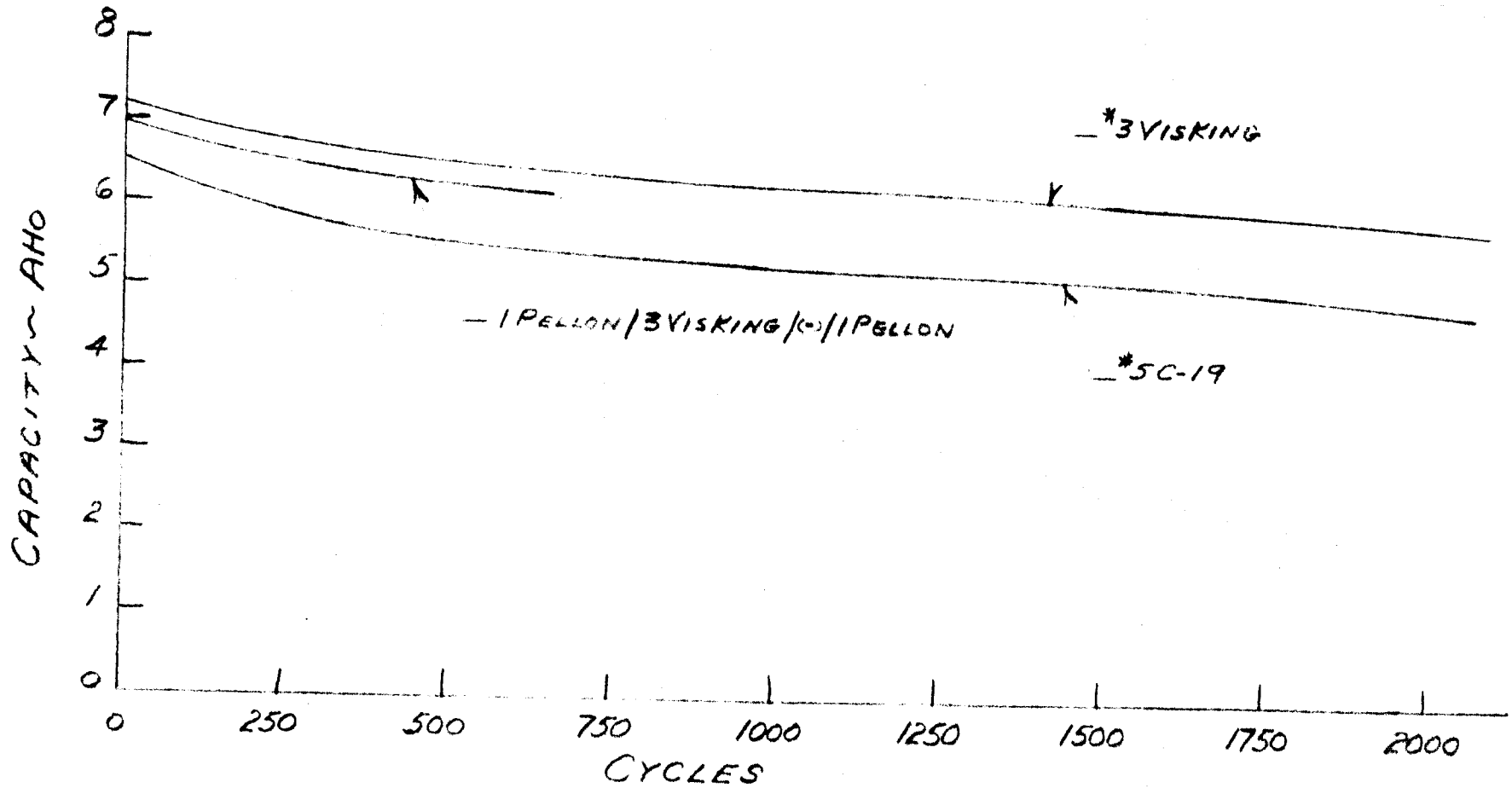
Fig. 4

CAPACITY MAINTENANCE - SINGLE CELLS
SHORT ORBIT REGIME

42% KOH

$I_C = 1.7A$ AREA = 20 in^2

$I_D = 3.0A$

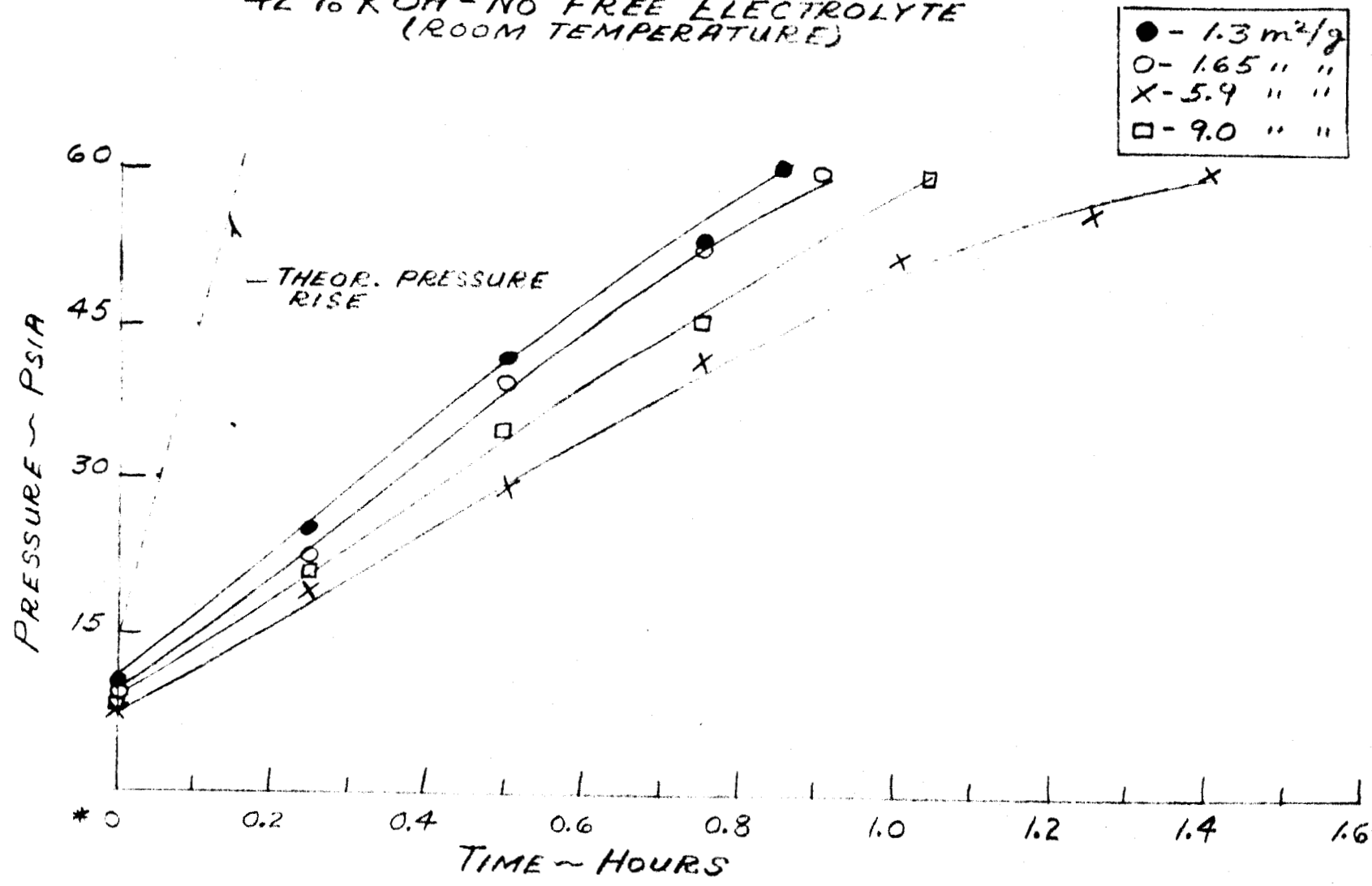


* CELLS CONTAINED A WOVEN POSITIVE SEPARATOR

PRESSURE BUILD-UP DURING OVERCHARGE

$I_C = 1.0A$

42% KOH - NO FREE ELECTROLYTE (ROOM TEMPERATURE)



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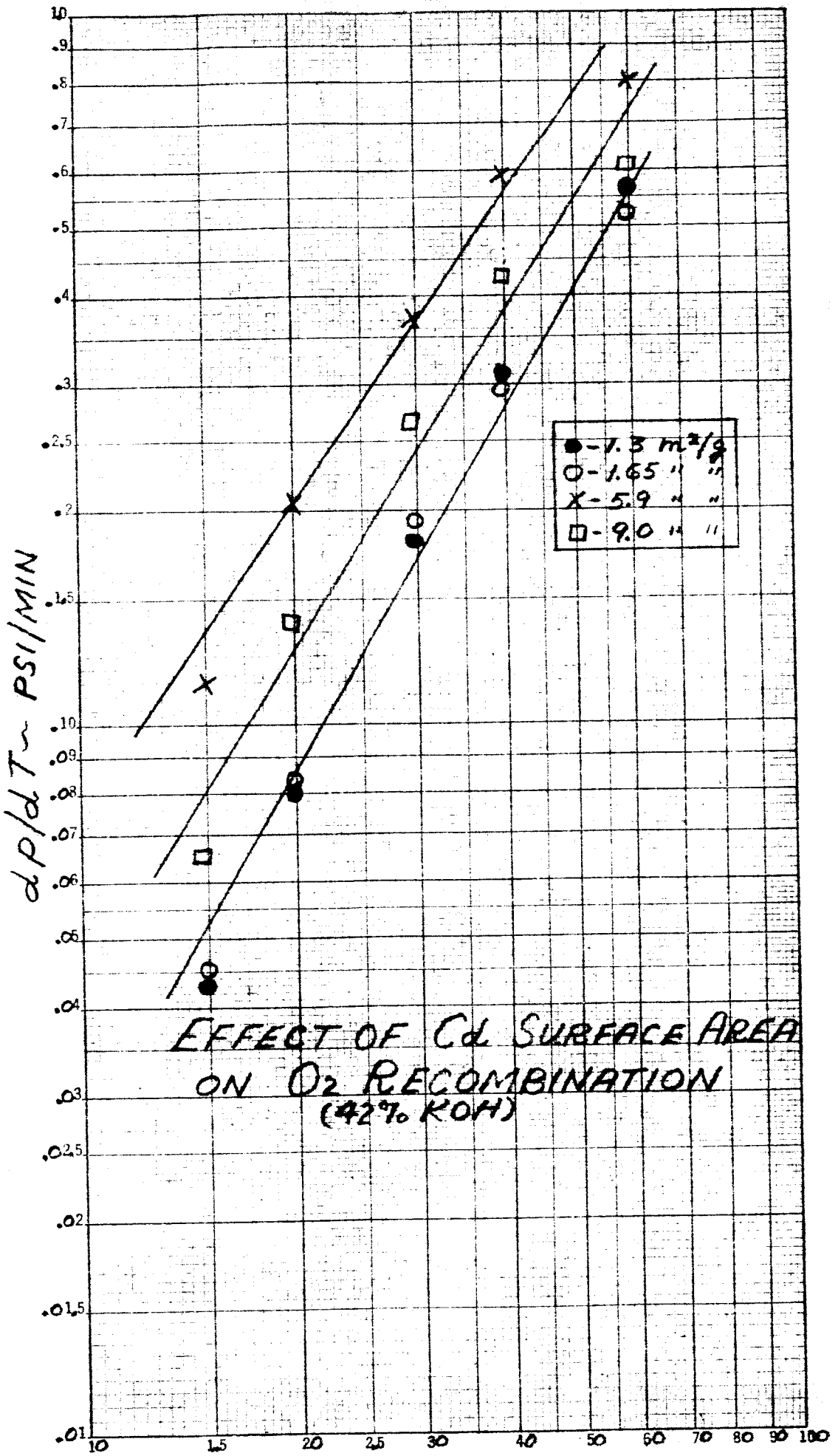
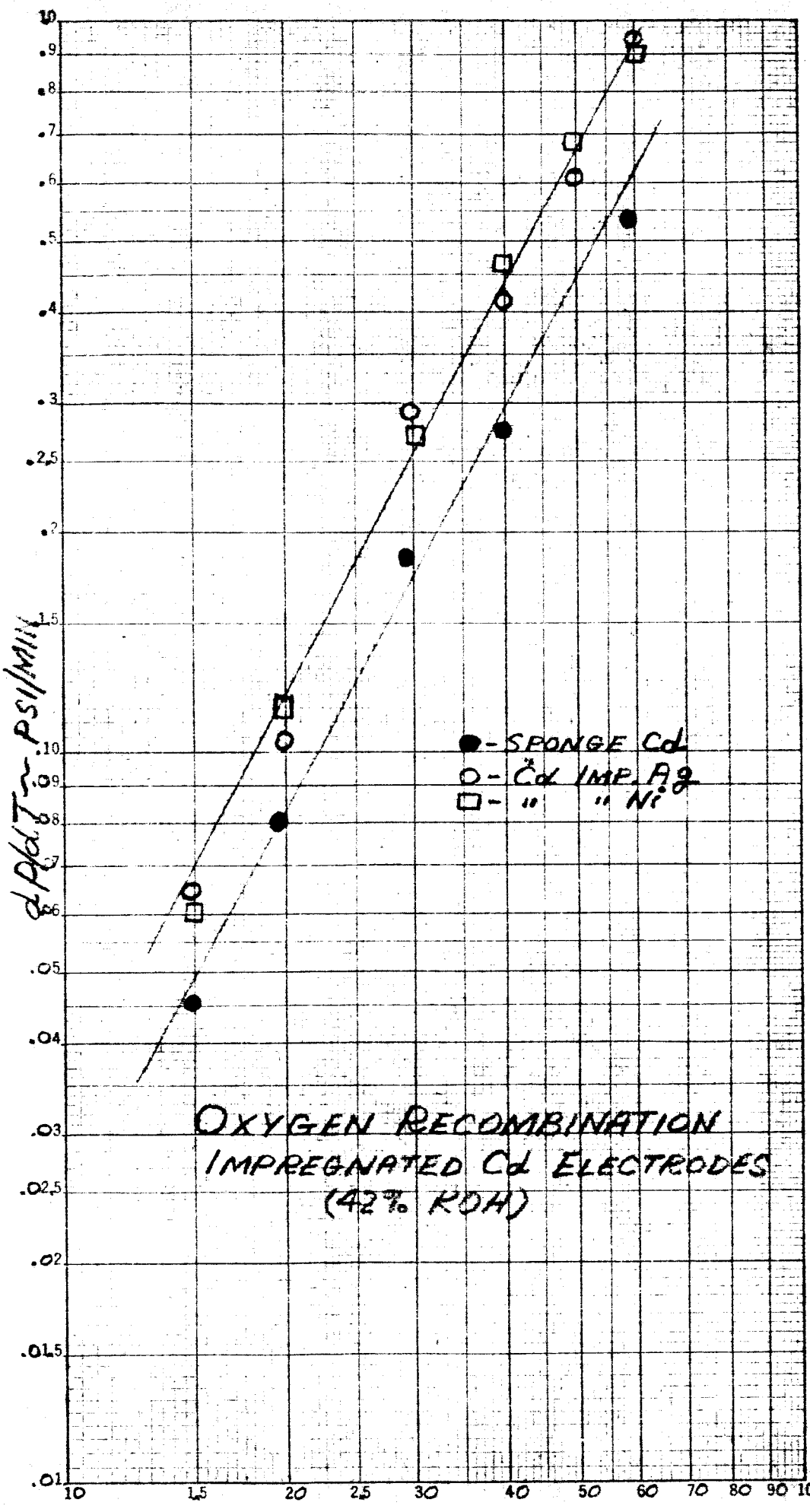
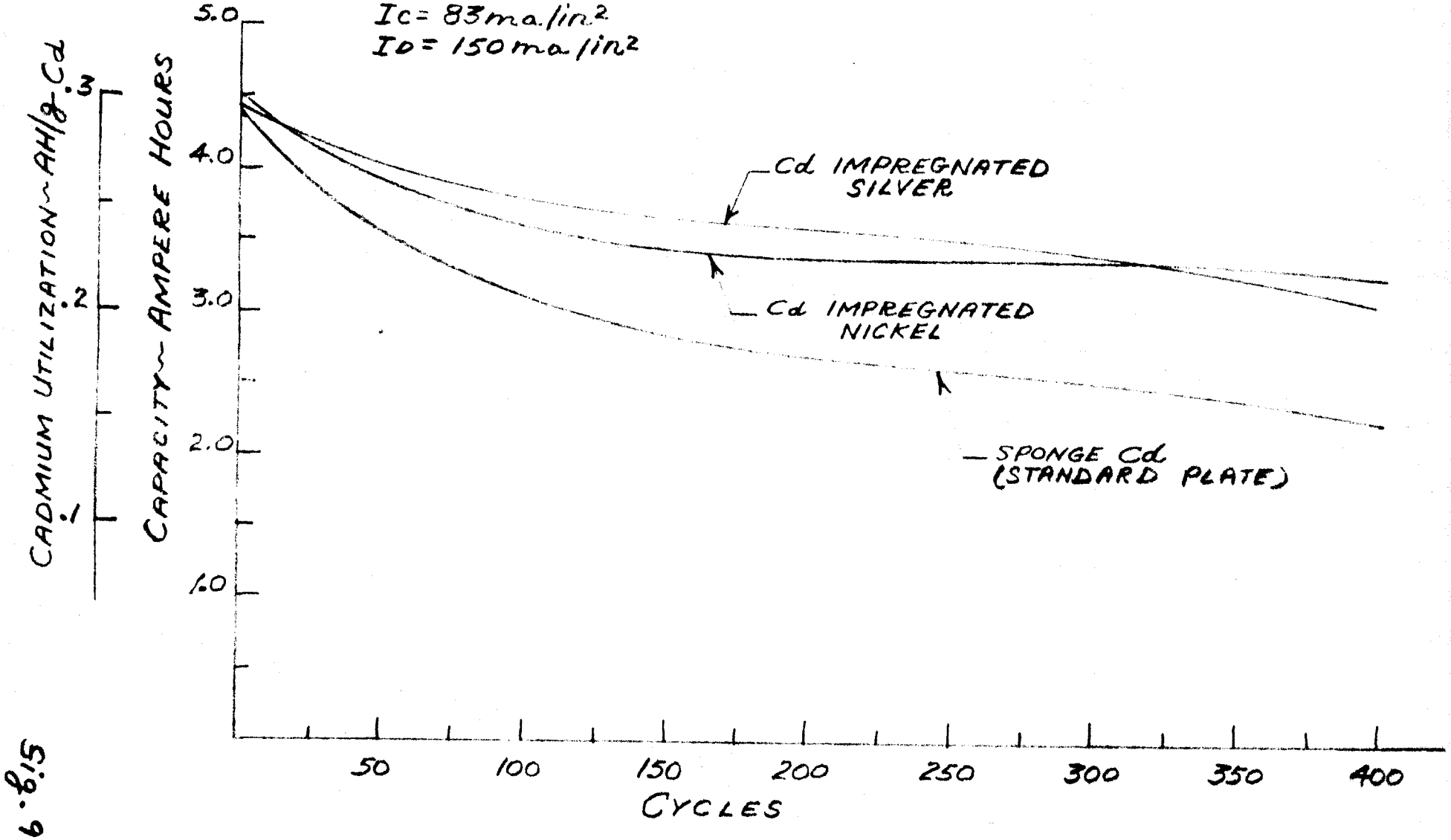
*O = BEGINNING OF OVERCHARGE - FROM 1.58 V/CELL





CAPACITY MAINTENANCE
SUPPORTED Cd ELECTRODES
DEEP CYCLES



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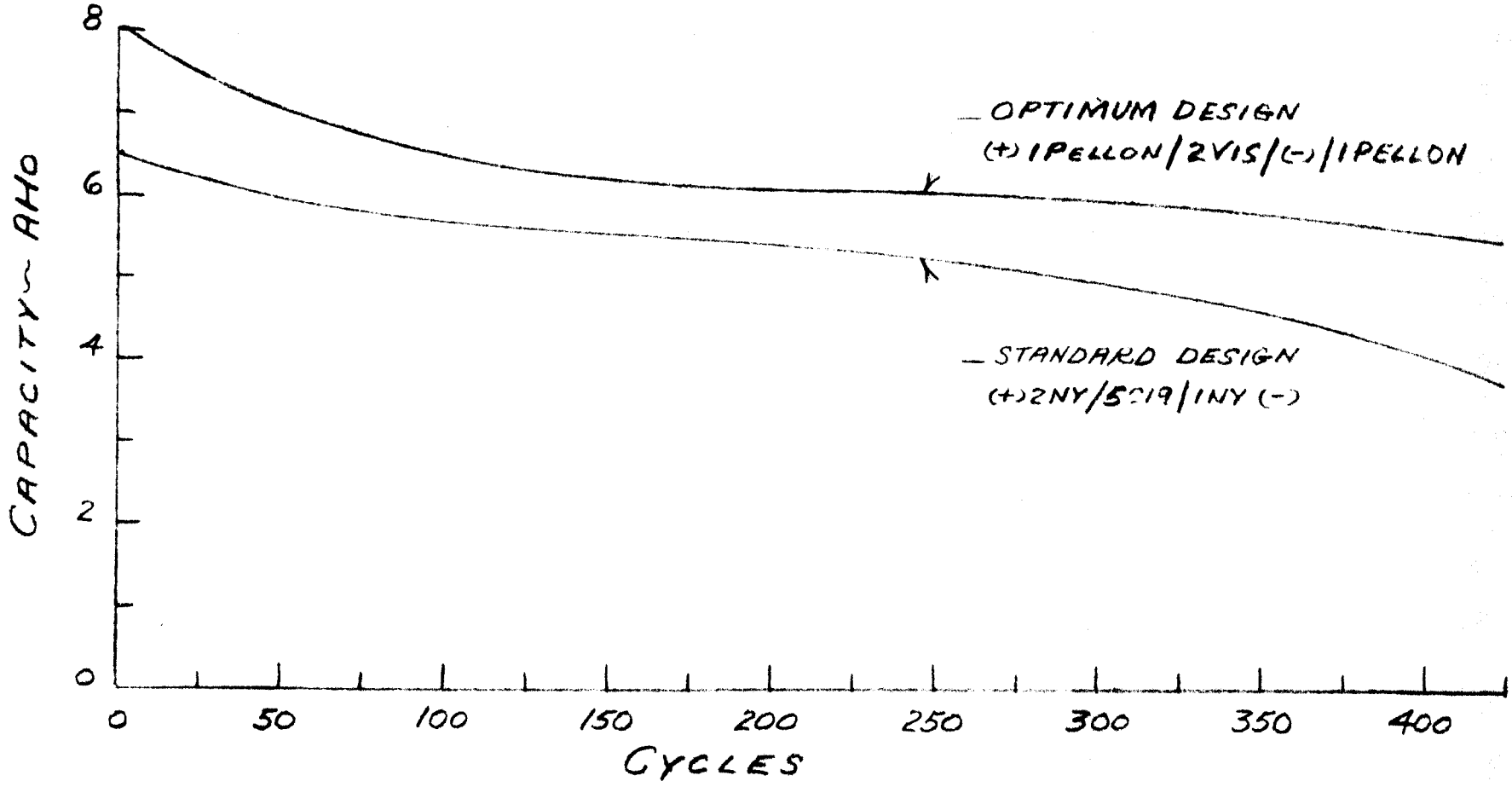
BATTERY CAPACITY MAINTENANCE
DEEP CYCLES

I_C = 1.7A → 8.2 VOLTS 23.5g Ag/CELL
I_D = 3.0A → 3.0 " 35.2g Cd/ "



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OXYGEN RECOMBINATION
42% KOH
(NO FREE ELECTROLYTE)

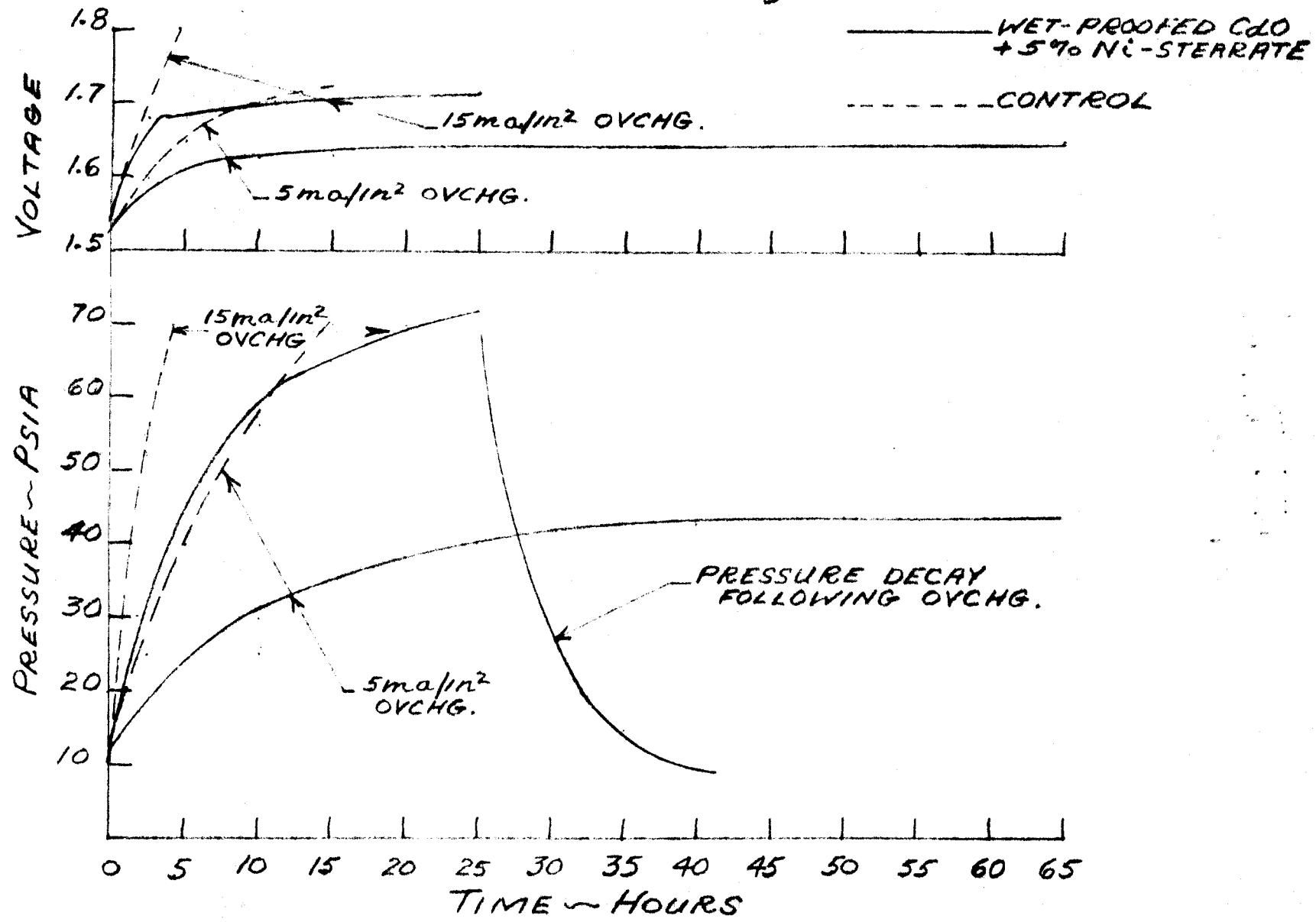

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TABLE I
BATTERY CONSTRUCTION PARAMETERS

	POSITIVE	NEGATIVE	SEPARATOR	ELECTROLYTE	Cd : Ag
BATT. A	4.8g Ag/cc 22.2g/CELL	STD. CdO MIX 30.7g CdO/CELL	(+) 1P-6/5C-19/1P-6	42% KOH – NO FREE ELEC.	1.3 : 1.0
BATT. B	4.2g Ag/cc 19.2g/CELL	STD. CdO MIX 33.2g CdO/CELL HALF END (–)	SAME AS BATTERY A		1.5 : 1.0
BATT. C	SAME AS IN BATT. B	RUGGEDIZED WET-PROOFED CdO 33.2g CdO/CELL HALF END (–)	SAME AS BATTERY A		1.5 : 1.0
BATT D	SAME AS BATTERY C		1-P6/3 VISKING/1-P6 (FIBROUS)	SAME AS BATTERY B	

TABLE II
DEEP CYCLE PERFORMANCE DATA (5-CELL BATTERIES)

I_C = 1.7A → 8.25 V
I_D = 3.0A → 3.0 V

TEMPERATURE	+40°C				"RT"				-10°C			
	AHi	AHo	$V_{P(I_D)}$	*dP/dT	AHi	AHo	$V_{P(I_D)}$	*dP/dT	AHi	AHo	$V_{P(I_D)}$	*dP/dT
BATT. A	6.55	6.5	1.08	0.65	6.3	6.3	1.07	0.38	3.35	3.25	.95	0.17
BATT. B	6.6	6.6	1.08	0.71	6.45	6.5	1.06	0.35	4.05	4.0	.94	0.15
BATT. C	6.85	6.9	1.07	1.15	6.7	6.7	1.06	0.72	3.85	3.8	.93	0.43
BATT. D	6.9	6.9	1.08	1.13	6.7	6.7	1.08	0.93	4.25	4.2	.98	0.45

* - O_2 PRESSURE DECAY - PSI/MIN AT 60 PSIA

TABLE V
PERFORMANCE DATA
NEGATIVE PLATE ADDITIVES

CYCLE NO	ID	CONTROL	1% MgO	5% MgO	1% Ni-St.	5% Ni-St	10% Fe_2O_3	20% Fe_2O_3	1% PVP
1	1.0A	6.6 AHo	6.55 AHo	6.2 AHo	6.4 AHo	6.0 AHo	6.2 AHo	5.45 AHo	5.7 AHo
2	2.0"	5.7 "	5.5 "	5.7 "	5.7 "	5.5 "	5.45 "	5.5 "	5.2 "
3	" "	5.9 "	5.9 "	5.9 "	5.5 "	5.8 "	5.5 "	5.2 "	5.3 "
4	3.0"	6.05 "	6.0 "	6.0 "	5.9 "	5.7 "	5.9 "	5.8 "	5.0 "
5	5.0"	6.25 "	6.3 "	6.25 "	6.2 "	6.0 "	6.1 "	5.8 "	4.7 "
6 -10°C	2.0"	3.95 "	4.05 "	4.0 "	4.0 "	3.75 "	4.45 "	4.30 "	4.0 "
7	" "	6.15 "	6.2 "	6.2 "	6.35 "	5.95 "	5.9 "	5.85	5.1 "
8 +40°C	" "	6.3 "	6.45 "	6.5 "	6.5 "	6.2 "	6.1 "	5.95 "	5.25 "
300	5.0"	5.45 "	5.15 "	5.22 "	5.85 "	5.45 "	5.33 "	5.21 "	4.9 "
301	2.0"	5.8 "	5.5 "	5.9 "	5.7 "	5.45 "	5.4 "	5.0 "	4.95 "
600	5.0"	5.2 "	5.25 "	5.35 "	5.0 "	4.7 "	5.0 "	4.7 "	CELL EXPLODED
601	2.0"	5.3 "	5.4 "	5.3 "	5.1 "	4.6 "	5.2 "	4.9 "	

$I_c = 83 ma/in^2$ (1.7A)

TABLE IX
CONSTANT POTENTIAL CHARGING
FLOAT VOLTAGE = 7.75 (1.55 V/CELL)

	AFTER 30 DAY FLOAT					AFTER 90 DAY FLOAT					AFTER 150 DAY FLOAT				
	CELL 1	CELL 2	CELL 3	CELL 4	CELL 5	CELL 1	CELL 2	CELL 3	CELL 4	CELL 5	CELL 1	CELL 2	CELL 3	CELL 4	CELL 5
BATTERY E PELLON ON POS. NEG. 4.8 g Ag/cc.															
PSIG	50	31	-10	-15	-19	28	32	-11	-9	-15	11	8	-2	-7	-20
VOLT	1.59	1.59	1.49	1.53	1.57	1.56	1.55	1.54	1.55	1.56	1.51	1.56	1.57	1.56	1.56
AHo	←		6.30		→	←		6.25		→	←		6.40		→
BATTERY F PELLON ON POS. NEG. 4.2 g Ag/cc.															
PSIG	30	-11	-16	-8	-2	13	16	21	-11	-7	14	3	-5	-11	-24
VOLT	1.55	1.56	1.55	1.54	1.55	1.55	1.57	1.59	1.53	1.55	1.58	1.54	1.51	1.56	1.55
AHo	←		6.20		→	←		6.0		→	←		6.15		→
BATTERY G STD. YS-56-4															
PSIG	75	68	82	57	80	37	26	42	21	33					
VOLT	1.55	1.56	1.55	1.55	1.55	1.58	1.53	1.70	1.45	1.49					
AHo	←		6.35		→	←		6.30		→					

NOTE: PRESSURE READINGS TAKEN PRIOR TO DISCHARGE